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Original Scientific Paper

A Gaussian-2 Study of Some Water-Catalyzed Reactions

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The Gaussian-2 computational method has been applied to study the following two reactions: (1) dihydrogen exchange between methanol and formaldehyde, and (2) hydrogen transfer in formic acid. In the investigation of these two reactions, the cases of both having and not having a catalytic water molecule have been examined. It has been found that, for the first reaction, the transition structures (TS) with and without the water molecule entail essentially the same barrier (117 kJ mol^{-1}). On the other hand, for the second reaction, the process involving the formic acid dimer TS has a barrier of 13 kJ mol^{-1}, while that involving a $HCOOH+H_2O$ TS has a barrier of 53 kJ mol^{-1}. The G2 method is suggested as a reliable tool to study reactions of this type.

INTRODUCTION

Water is the most common and most abundant of all solvents and reactions often take place in an aqueous medium. In addition, water may sometimes play a catalytic role in the reaction. In this work, we apply high-level theoretical methods to determine whether or not a given reaction is catalyzed by water. The reactions investigated are: (1) dihydrogen exchange between methanol and formaldehyde, and (2) hydrogen transfer in formic acid.

These reactions, except for process (2b), have already been examined theoretically.[1,2] However, these studies have been carried out at different *ab initio* levels and hence it is difficult to compare their results. In this work,

we have studied these reactions using the Gaussian-2 (G2) model so that the results of one reaction may be constrasted with those of the other.

$$CH_2O + CH_3OH \xrightarrow{TS(CH_2O+CH_3OH)} CH_3OH + CH_2O, \quad (1a)$$

$$CH_2O + CH_3OH + H_2O \xrightarrow{TS(CH_2O+CH_3OH+H_2O)} CH_3OH + CH_2O + H_2O, \quad (1b)$$

$$2HCOOH \longrightarrow (HCOOH)_2 \xrightarrow{TS[(HCOOH)_2]} 2HCOOH, \quad (2a)$$

$$HCOOH + H_2O \longrightarrow HCOOH \cdot H_2O \xrightarrow{TS(HCOOH+H_2O)} HCOOH + H_2O. \quad (2b)$$

The present work is part of a systematic study of water-catalyzed reactions using the G2 method. In a recent report by Morokuma and Muguruma,[3] it has been found that the hydrolysis of SO_3 to H_2SO_4 is catalyzed by an additional water molecule. Specifically, the uncatalyzed reaction has an activation barrier of 134.7 kJ mol^{-1}, as compared to the barrier of 48.1 kJ mol^{-1} for the catalyzed reaction. The barriers were calculated at the MP4SDQ/6-311+G(d,p)//MP2(FC)/6-311+G(d,p) level. Inspired by this work, we proceeded to investigate the hydrolysis of SO_2, with and without a catalytic water molecule, at the G2 level. It has been found that the uncatalyzed reaction has a barrier of 141.8 kJ mol^{-1}, which is reduced to 83.7 kJ mol^{-1} with one catalytic water. These results have been published elsewhere.[4]

COMPUTATIONAL METHODS

All calculations were carried out with the Gaussian 94 program package.[5] The G2 energies of the various species were computed in the standard way,[6] while enthalpy correction at 1 atm and 298 K were computed using HF/6-31G(d) frequencies in the harmonic approximation with the scaling factor[6] of 0.8929. The G2 energy is an approximation of the QCISD(T)/6-311+G(3df,2p) calculation. Such an approximation requires frozen-core single-point calculations at the QCISD(T)/6-311G(d,p), MP4/6-311G(d,p), MP4/6-311+G(d,p), MP4/6-311G(2df,p), and MP2/6-311+G(3df,2p) levels, all based on the MP2(full)/6-31G(d) geometry.

RESULTS AND DISCUSSION

Total G2 energies at 0 K (E_0) and enthalpies at 298 K (H_{298}) are summarized in Table I. The relative enthalpies on the potential energy surfaces

studied are displayed pictorially in Figure 1. Molecular structures, optimized at the MP2(Full)/6-31G(d) level, of important spieces on the potential energy surfaces studied are presented in Figure 2.

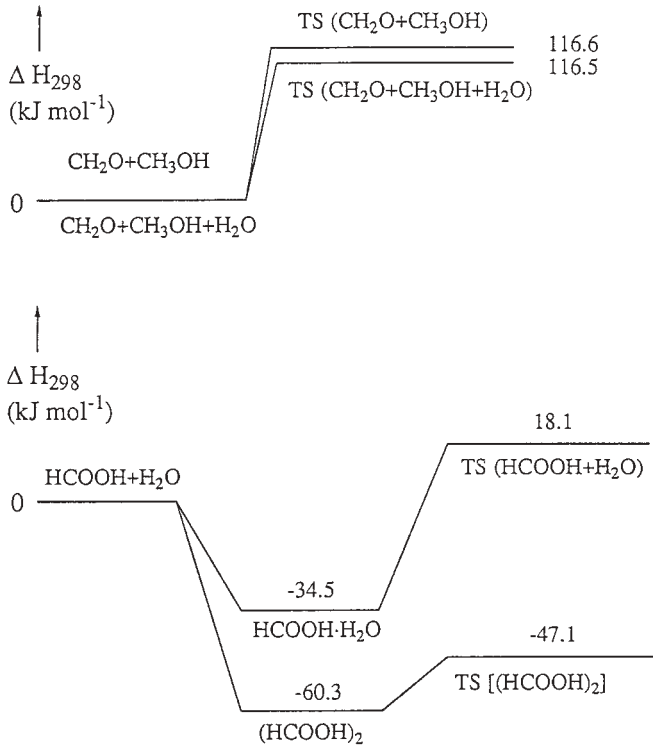
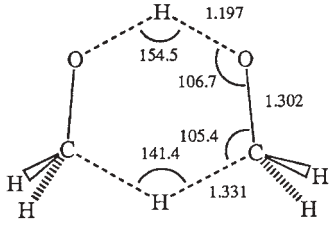


Figure 1. G2 enthalpy profile for the reactions studied.

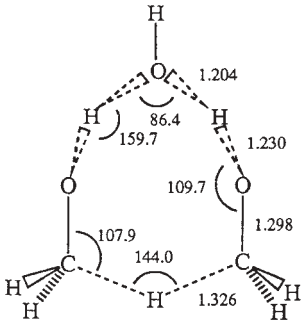
Dihydrogen Exchange between Methanol and Formaldehyde

As mentioned previously, this reaction has been investigated by McKee and co-workers.[1] In the absence of water, this process takes place *via* the transition structure TS(CH_2O+CH_3OH). The MP2(Full)/6-31G(d) structure of TS(CH_2O+CH_3OH), as shown in Figure 2, is very similar to the HF/6-31G(d) structure reported by McKee *et al.*[1] Hydrogen transfer between the oxygen atoms is almost linear (154.5°), while the hydrogen shift between the two carbons is more bent (141.4°). The G2 enthalpy barrier at 298 K for this process is 116.6 kJ mol^{-1}, as compared to the MP2/6-31G(d)//HF/6-31G(d) (at 0 K) result of 130.5 kJ mol^{-1} reported by McKee and co-workers.[1]

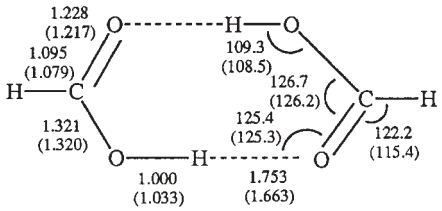
When water is also a participant in the exchange process, the TS involved is TS(CH_2O+CH_3OH+H_2O), as shown in Figure 2. While this struc-



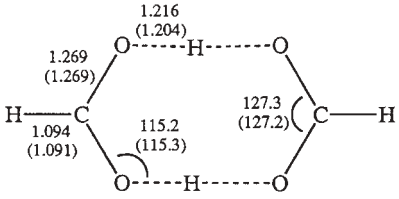
TS (CH_2O+CH_3OH) , C_{2v}



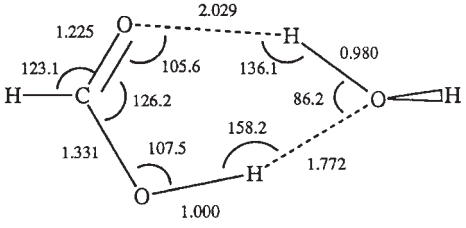
TS (CH_2O+CH_3OH+H_2O) , C_s



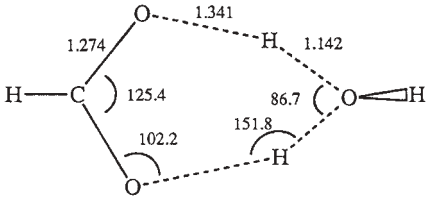
$(HCOOH)_2$, C_{2h}



TS [$(HCOOH)_2$] , D_{2h}



$HCOOH{\cdot}H_2O$, C_1



TS (HCOOH+H_2O) , C_s

Figure 2. Molecular structures of species relevant to the reactions studied. Selected geometric parameters are at the MP2(Full)/6-31G(d) level. Those in brackets are the MP2(Full)/6-31G(d,p) parameters.

ture is similar to the HF/6-31G(d) geometry reported in Ref. 1, it is noted that the HF structure has two imaginary vibrational frequencies, while the MP2 structure has only one, as it should be the case. As noted in Ref. 1, three bonds are broken simultaneously in this TS. The G2 enthalpic barrier for this process is calculated to be 116.5 kJ mol^{-1}, essentially the same as that for the case without the water molecule. For comparison, the MP2/6-31G(d)//HF/6-31G(d) (at 0 K) barrier is 126.8 kJ mol^{-1}. Thus, we may draw a conclusion similar to that of McKee *et al.*:[1] The catalytic water molecule leads to an enthalpic barrier similar to the uncatalyzed mechanism.

Hydrogen Transfer in Formic Acid

In the absence of water, two formic acid molecules form a dimer, $(HCOOH)_2$, with C_{2h} symmetry. The double hydrogen transfer takes place via the highly symmetrical transition structure TS[$(HCOOH)_2$] with D_{2h} symmetry. These two processes, dimerization and two-hydrogen transfer of formic acid, have been studied extensively by calculation.[2,7] In Kim's study,[2] these two processes have been investigated using the G2* model. In this model, geometry optimization and vibrational frequency calculations are carried out at the MP2(Full)/6-31G(d,p) level, instead of the MP2(Full)/6-31G(d) level in the regular G2 theory. Kim's optimized geometrical parameters are also included in Figure 2 for easy comparison. As it can be seen from this figure, the only major difference in the dimer $(HCOOH)_2$ is in the hydrogen bond O...H bond length, the G2* and G2 results are 1.711 Å and 1.753 Å, respectively, as compared to the experimental result of 1.663 Å. As for the structure of TS[$(HCOOH)_2$], the G2 and G2* geometries are essentially the same.

Attention is now turned to the energetics of these two processes. At the G2 level, the dimerization enthalpy and enthalpic barrier at 298 K (ΔH_{298}) are calculated to be 60.3 and 13.2 kJ mol^{-1}, respectively. Note that the barrier is calculated by considering the dimer $(HCOOH)_2$ as »reactants«. In Kim's work, only the energy changes at 0 K (ΔE_0) are reported: the G2* dimerization energy and barrier height are 59.5 and 21.8 kJ mol^{-1}. From Table I, we can readily calculate the corresponding G2 values at 0 K: 59.7 and 16.2 kJ mol^{-1}, respectively. Experimentally, the dimertization energy has been measured to be 61.9 ± 2.1[8], 59.0 ± 6.3[9] and 48.9 ± 0.4[10] kJ mol^{-1}. Bearing in mind that the generally accepted G2 accuracy is ±10 kJ mol^{-1}, the G2 results reported here should be termed satisfactory.

When water is present, formic acid and water form a stable complex $HCOOH{\cdot}H_2O$ with C_1 symmetry. From the structure shown in Figure 1, it is seen that the ring portion of this complex is essentially planar (sum of internal angles is 719.8°). The G2 complexation enthalpy is 34.5 kJ mol^{-1}.

TABLE I

Gaussian-2 total energies at 0 K (E_0) and enthalpies at 298 K (H_{298}) and relative enthalpies ΔH_{298} at 298 K for the reactions studied in this work

Species	Symmetry	E_0(hartree)	H_{298}(hartree)	H_{298}(kJ mol^{-1})
$CH_2O + CH_3OH$	C_{2v}; C_s	–299.87381	–299.86570	0
$TS(CH_2O + CH_3OH)$	C_{2v}	–299.82700	–299.82129	116.6
$CH_2O + CH_3OH + H_2O$	C_{2v}; C_s; C_{2v}	–306.20587	–306.19398	0
$TS(CH_2O + CH_3OH + H_2O)$	C_s	–306.15699	–306.14960	116.5
2HCOOH	C_s	–379.03296	–379.02468	0
$(HCOOH)_2$	C_{2h}	–379.05570	–379.04763	–60.3
$TS[(HCOOH)_2]$	D_{2h}	–379.04953	–379.04263	–47.1
$HCOOH + H_2O$	C_s; C_{2v}	–265.84854	–265.84062	0
$HCOOH \cdot H_2O$	C_1	–265.86069	–265.85385	–34.5
$TS(HCOOH + H_2O)$	C_s	–265.83895	–265.83372	18.1

The transition structure for the dihydrogen transfer between formic acid and water is TS(HCOOH+H_2O) with C_s symmetry. Again, the ring portion of this structure is practically planar (sum of internal angles is 720.1°). The G2 enthalpic barrier is 52.6 kJ mol^{-1}, much larger than the barrier for the uncatalyzed process. [Again, the barrier is calculated by considering the complex $HCOOH \cdot H_2O$ as »reactants«.] Hence, while water provides an alternative pathway for the hydrogen transfer in formic acid, this pathway is not energetically favorable.

CONCLUSION

To summarize, it is found that, for the dihydrogen exchange reaction between methanol and formaldehyde, the processes with and without a catalytic water molecule entail a practically identical G2 barrier (117 kJ mol^{-1}). Meanwhile, for the hydrogen transfer process in formic acid, that involving the $(HCOOH)_2$ dimer TS has a barrier of 13 kJ mol^{-1}, while that involving a $HCOOH + H_2O$ TS has a barrier of 53 kJ mol^{-1}. The G2 results reported in this work agree with the available experimental data and other theoretical results. It is suggested that the G2 method is an effective and reliable tool to study such catalytic reactions. Indeed, we have already carried out simi-

lar calculations for the hydrolysis of SO_2, with and without a catalytic water molecule.[4] Studies of other catalytic reactions are being planned.

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SAŽETAK

Istraživanje nekih vodom kataliziranih reakcija metodom Gaussian-2

Wai-Kee Li

Metoda Gaussian-2 primijenjena je za istraživanje slijedećih reakcija: (1) razmjenu vodika između molekula metanola i formaldehida i (2) prijenos vodika kod mravlje kiseline. Reakcije su proučavane sa i bez prisutnosti katalitičke molekule vode. Pokazano je da je katalitički utjecaj molekule vode zanemariv za reakciju razmjene vodika između molekula metanola i formaldehida, tj. njihove reakcijske su barijere gotovo jednake (117 kJ mol-1). Za prijenos vodika kod mravlje kiseline dobivene su reakcijske barijere od 13 kJ mol^{-1} za dimer mravlje kiseline i 53 kJ mol^{-1} za reakciju mravlje kiseline i vode. Pokazano je da je metoda Gaussain-2 pouzdana za istraživanje navedenih reakcija.